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EFFECTS OF IMPURITIES ON CARRIER LIFETIME IN BULK SOLAR-CELL MATERIAL

QUARTERLY REPORT

NOVEMBER 1968

Letter Contract No. 952256

NORTHROP CORPORATE LABORATORIES
3401 West Broadway
Hawthorne, California 90250

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NOTICE

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NEW TECHNOLOGY

All technological developments to date are reported herein. They are considered to be unreportable under the instructions of NHB 2170.2 dated October 1966.

ABSTRACT

Lifetime samples have been prepared from crystals containing Na, Be, Cl, and Al dopants and from B- and P-doped crystals containing very high oxygen concentrations. Preliminary measurements indicate that neither the Be nor the Cl-doped material will be satisfactory for lifetime studies because of the poor quality of the material. Studies of lifetime degradation in various materials by 2 MeV electrons and the subsequent recovery of lifetime by thermal annealing indicate that both the damage rate and annealing behavior are strongly dependent upon the type of impurities in the sample. Isochronal annealing studies were performed on five identical samples which had been irradiated with a relatively low dose of Co^{60} γ-rays. Although the samples had been completely annealed following a previous irradiation in which each received a different dose, the amount of recovery during the second anneal was dependent upon the dose received during the first exposure. An attempt to distribute Li uniformly throughout a large bulk sample by diffusion in an inert atmosphere proved unsuccessful and indicates that the apparent loss of Li from samples after prolonged heating is due to precipitation rather than to evaporation from the surface.

INTRODUCTION

This report describes some preliminary studies of the effect of certain non-conventional dopant impurities or high oxygen concentration on the carrier lifetime degradation of silicon by 2 MeV electrons. These studies were undertaken to investigate the recombination properties of these dopants and to determine whether the use of such impurities might permit the construction of solar cells and other devices more resistant to radiation than those currently employed. In addition to these studies, the recovery of lifetime by thermal annealing following 2 MeV electron irradiation and Co^{60} γ irradiation is being investigated to further evaluate possible impurity effects.

TECHNICAL DISCUSSION

SAMPLE PREPARATION

All of the crystals to be used in this study have been received and a major portion of the effort during this quarter was devoted to sample preparation and preliminary lifetime measurements. Samples containing excess oxygen in addition to the normal phosphorus and boron dopants, control samples containing the same dopants but less oxygen, Al-doped samples grown by two different techniques (different oxygen contents) and Na-doped samples had reasonably long lifetimes and should prove useful for this study. The Cl- and Be-doped materials, on the other hand, do not appear to be useful. Both of these crystals are p-type and supposedly contain approximately 10^{15} dopant atoms cm^{-3}. Although we have not been able to apply ohmic contacts to Cl-doped samples to determine the resistivity accurately, preliminary resistance measurements indicate that it is extremely high ($\sim 2.8 \times 10^{4}$ ohm-cm). In contrast, the Be-doped crystal has a low resistivity (0.86 ohm-cm) but the lifetime is on the order of only 0.2 μs. This crystal is also p-type.

Attempts were made to increase the lifetime of the Be-doped material by various heat treatments. It was hoped that such treatments would cause excess Be to precipitate in the crystal and result in an increase in both the lifetime and resistivity. Although anneals at 700°C produced very large resistivity changes in this material, these treatments unfortunately did not produce the desired lifetime improvement.

LIFETIME DEGRADATION BY 2 MEV ELECTRONS

Eighteen samples representing seven different crystals were irradiated with 2 MeV electrons to study lifetime degradation and recovery in these materials. During each exposure, two samples were irradiated simultaneously using two electron pulses for a total exposure of 6.25×10^{13} electrons cm^{-2} (average energy 1.7 MeV). After the first pulse, the samples were reversed, rotated, and interchanged to provide

more uniform penetration of the beam and to equalize the dose received by the two samples. The results are summarized in Table I which shows the initial and post-irradiation lifetimes and the damage constant for each sample. The damage constant, K, is defined through the relationship

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{\phi}{K}$$

where τ_0 and τ are the initial and post-irradiation lifetimes, respectively and ϕ is the electron fluence. If the lifetimes are expressed in microseconds, K represents the fluence required to reduce the lifetime of an initially perfect sample ($\tau_0 = \infty$) to 1 μs and is thus an indication of the radiation resistance of the sample.

The sample designation scheme employed in Table I is as follows: the first letter (S, T, M, or G) indicates the crystal manufacturer (Semi Elements, Texas Instruments, Merck, or General Electric, respectively). The second letter (C, V, L, or F) denotes the crystal growth technique (Czochralski, Vacuum-float-zone, LOPEX, or Float-zone in an inert atmosphere). The remaining symbols indicate the dopant impurity and the initial resistivity measured at 30°C. Samples designated SCPO and SCBO contained excess oxygen in addition to the respective phosphorus and boron dopants.

Examination of the data in Table I indicates that the damage constants of samples containing excess oxygen are consistently smaller than those of similar samples which do not contain oxygen as an added impurity. This result is quite surprising since we have previously found that samples pulled from a quartz crucible (Czochralski technique) and consequently containing up to $\sim 10^{18}$ oxygen atoms cm^{-3} exhibited larger damage constants following 10 MeV electron irradiation than did oxygen-free ($< 10^{17}$ cm^{-3}) samples. The relatively large damage constants exhibited by the two GFA1 samples indicate that this material is more radiation resistant than any of the other materials. However, the large scatter in the damage rates for identical samples prevents a detailed assessment of any other impurity effects. Part of this scatter is due to significant trapping observed in some of the materials either before or after irradiation. Such trapping causes the photoconductivity to

TABLE 1. LIFETIME CHANGES PRODUCED IN SILICON BY 2 MEV ELECTRON IRRADIATION

SAMPLE		τ μs	τ_0 μs	K $e/cm^2 \mu s \times 10^{14}$
SCPO	4.0	1.73	20.5	1.18
SCPO	3.9	2.11	18.0	1.49
SCPO	3.9	2.14	21.6	1.49
TCP	10.5	5.76	577	3.60
TCP	12.8	6.49	534	4.11
SCBO	6.7	1.73	14.7	1.22
SCBO	6.7	2.02	20.2	1.40
SCBO	7.0	2.08	17.2	1.48
TCB	10.3	5.63	225	3.61
TCB	9.9	2.89	199	1.83
MVB	8.1	5.05	112	3.31
MVB	8.4	9.96	137	6.71
MVB	8.3	9.24	115	6.28
TLA1	6.4	4.26	118	2.76
TLA1	6.5	6.13	144	4.00
TLA1	6.6	6.64	136	4.36
GFA1	10.4	16.45	171	11.41
GFA1	10.1	14.25	162	9.77

decay non-exponentially and complicates the lifetime measurements. Additional measurements will be performed to improve the statistics.

ISOCHRONAL ANNEALING STUDIES ON 2 MEV ELECTRON-IRRADIATED SAMPLES

Six of the samples indicated in Table I have been isochronally annealed between 72°C and 253°C and the results indicate that lifetime recovery following 2 MeV electron irradiation is strongly dependent upon the impurities in the sample. Phosphorus- and boron-doped samples containing excess oxygen (samples designated SGPO and SGBO in Table I) exhibited little or no lifetime recovery after annealing at 253°C while samples containing the same dopants but less oxygen did recover partially at this temperature. A single GFA1 sample, on the other hand, recovered almost completely. One vacuum-float-zone sample containing boron was annealed and it exhibited reverse annealing behavior throughout the annealing cycle. We have observed similar behavior in this material following 10 MeV-electron irradiation.

DOSE DEPENDENCE OF LIFETIME ANNEALING IN Co^{60} GAMMA-IRRADIATED SILICON

The five lifetime samples which were isochronally annealed following exposure to different Co^{60} γ-ray doses (see Figure 3 of the first Quarterly Report - August 1968) were re-irradiated with a relatively low dose ($\sim 1.40 \times 10^{7}$ R). The samples were annealed after the second irradiation and the amount of damage remaining at high temperature was again dependent upon the dose received in the first irradiation (or the total dose). This result is surprising because less than 1% of the lifetime damage produced in the first irradiation was present after the first anneal. The existence of this dose dependence suggests that attempts to provide moderate-temperature annealing cycles for solar cells in a use environment may prove unsuccessful.

LITHIUM DIFFUSION STUDIES

Attempts to distribute Li uniformly throughout bulk samples using various heat treatments have been continued. Since previous heat treatments performed in vacuum proved only partly successful and indicated

that Li was being lost by either precipitation or evaporation from the surface, a subsequent treatment was performed with the sample in an argon atmosphere to retard possible evaporation of Li from the surface. The resistivity profile of this sample was essentially identical to that of a similar sample which was given the same heat treatment but in vacuum. These similar results indicate that the apparent loss of Li as evidenced by the increase in resistivity of samples after prolonged heating is due to precipitation rather than to evaporation from the surface and thus can not be influenced by the use of an inert gas atmosphere.

The results to date indicate that regions of relatively uniform resistivity ~ 3 mm wide can be obtained by diffusing lithium into ~ 7 mm thick silicon slabs and employing certain heat treatments. Since these regions are of approximately the same thickness as the samples to be used in this study, suitable samples can probably be obtained by bisecting thicker slabs following the appropriate diffusion cycle. A high resistivity n-type (phosphorus-doped) crystal was received recently and will be used to produce such samples.

CONCLUSIONS AND FUTURE PLANS

Results of measurements performed on lifetime samples containing Be and Cl indicate that these materials cannot be used for lifetime studies. Since we were able to obtain these materials from only one supplier and only on a best effort basis, we do not intend to purchase additional crystals for further studies.

Studies of lifetime degradation by 2 MeV electrons will be extended to include Na-doped samples and additional samples of various materials will be included to improve the statistics of the damage constant determinations. Smaller electron doses will be employed in these studies to improve the accuracy of the post-irradiation lifetime measurements in some of the materials. These studies will also be extended to Li-doped material as soon as suitable samples are obtained.

Isochronal annealing studies will be performed on at least one sample from each crystal used in these experiments. Studies performed to date indicate that the annealing behavior is strongly dependent upon both the dopant impurity and the oxygen concentration.

The behavior of FZ Al-doped Si is most encouraging. The excellent starting characteristics of this material indicate it would be satisfactory for solar cell fabrication, while the decreased degradation rate, compared to other materials, appears significant. Studies will continue to ascertain the stability and recombination characteristics of defects in Al-doped Si.